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(03.07.99)
03 July 1999TITLE OF INVENTION
METHOD FOR THE SELECTIVE COATING OF CERAMIC SURFACE AREAS

APPLICANT(S) FOR DO/EO/US

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Applicant(s) herewith submit to the United States Designated/Elected Office (DO/EO/US) the following items and other information

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) immediately rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) (unsigned).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☒ A substitute specification and a marked up version thereof.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information: International Search Report, International Preliminary Examination Report and Form PCT/RO/101.

Express Mail No. EL244510277

SIGNATURE

Richard L. Mayer, Reg. No. 22,490
NAME

DATE _____

[10191/2180]

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s) : Walter ROETHLINGSHOEFER et al.
Serial No. : To Be Assigned
Filed : Herewith
For : METHOD FOR THE SELECTIVE COATING OF CERAMIC
SURFACE AREAS
Art Unit : To Be Assigned
Examiner : To Be Assigned

Assistant Commissioner for Patents
P.O. Box 2327
Arlington, VA 22202

**PRELIMINARY AMENDMENT AND
37 C.F.R. § 1.125 SUBSTITUTE SPECIFICATION STATEMENT**

SIR:

Please amend without prejudice the above-identified application before examination, as set forth below.

IN THE SPECIFICATION AND ABSTRACT:

In accordance with 37 C.F.R. § 1.121(b)(3), a Substitute Specification (including the Abstract, but without claims) accompanies this response. It is respectfully requested that the Substitute Specification (including Abstract) be entered to replace the Specification of record.

IN THE CLAIMS:

On the first page of claims, first line, change "What is claimed is:" to
--WHAT IS CLAIMED IS:--.

Please cancel, without prejudice, claims 1 to 16 in the underlying PCT application.

8244510277

Please add the following new claims:

--17. (New) A method for treating a surface of a ceramic hybrid substrate including ceramic surface areas and metallic surface areas, comprising the step of esterifying the ceramic surface areas.

18. (New) The method according to claim 17, further comprising the step of treating the ceramic surface areas with a solution including organic constituents tailored to the ceramic hybrid substrate.

19. (New) The method according to claim 18, wherein the ceramic hybrid substrate is manufactured on the basis of silicon and the solution includes silicon.

20. (New) The method according to claim 18, wherein the solution includes a siloxane solution.

21. (New) The method according to claim 20, wherein the solution includes between 0.1 and 1% of siloxane and between 99 and 99.9% of isopropanol, relative to 100% total volume.

22. (New) The method according to claim 18, wherein the treating step includes the substep of applying the solution by dip coating.

23. (New) The method according to claim 18, wherein the treating step includes the substep of applying the solution by spraying.

24. (New) The method according to claim 18, further comprising the step of removing excess solution mechanically.

25. (New) The method according to claim 24, wherein the removing step includes the substep of wiping off the excess solution.

26. (New) The method according to claim 24, wherein the removing step includes the substep of blowing off the excess solution.

27. (New) The method according to claim 18, further comprising the step of heat-treating surface contacted by the solution in the treating step.

28. (New) The method according to claim 27, wherein the surface is heat-treated in the heat-treating step at a temperature of approximately 100°C.

29. (New) The method according to claim 27, wherein the heat-treating step is performed for a period of between 0.4 and 0.6 hours.

30. (New) The method according to claim 27, further comprising the step of removing solution constituents not crosslinked after the heat-treating step.

31. (New) The method according to claim 30, wherein the removing step includes the substep of washing off the solution constituents not crosslinked.

32. (New) A ceramic hybrid substrate, comprising:
a surface including ceramic surface areas and metallic surface areas, wherein the ceramic surface areas are esterified.--.

REMARKS

This Preliminary Amendment cancels, without prejudice, claims 1 to 16 in the underlying PCT Application No. PCT/DE00/02023 and adds new claims 17 to 32. The new claims conform the claims to U.S. Patent and Trademark Office rules and do not add new matter to the application.

In accordance with 37 C.F.R. § 1.121(b)(3), the Substitute Specification (including the Abstract, but without the claims) contains no new matter. The amendments reflected in the Substitute Specification (including Abstract) are to conform the Specification and Abstract to U.S. Patent and Trademark Office rules or to correct informalities. As required by 37 C.F.R. § 1.121(b)(3)(iii) and § 1.125(b)(2), a Marked-Up Version of the Substitute Specification comparing the Specification of record and the Substitute Specification also accompanies this Preliminary Amendment. Approval and entry of the Substitute Specification (including Abstract) is respectfully requested.

The underlying PCT Application No. PCT/DE00/02023 includes an International Search Report, dated October 27, 2000. The Search Report includes a list of documents that were uncovered in the underlying PCT Application. A copy of the Search Report accompanies this Preliminary Amendment.

The underlying PCT application also includes an International Preliminary Examination Report, dated August 13, 2001. An English translation of the International Preliminary Examination Report accompanies this Preliminary Amendment.

Applicants assert that the subject matter of the present application is new, non-obvious, and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully Submitted,

KENYON & KENYON

Dated: January 3, 2002

By:

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CUSTOMER NO. 26646

METHOD FOR THE SELECTIVE COATING OF CERAMIC SURFACE AREAS

FIELD OF THE INVENTION

The present invention relates to a method for treating the surface of a ceramic hybrid substrate including ceramic surface areas and metallic surface areas.

BACKGROUND INFORMATION

The use of ceramic (glass ceramic) hybrid substrates is conventional, for example, in the construction of electrical circuit arrangements. Such electrical circuit arrangements are used in various industrial areas, for example, in the area of motor vehicle electronics for engine control, anti-lock braking control, etc. The ceramic hybrid substrates contain processed electronic components and metallic conducting tracks, via which contacting of the hybrid substrates can occur. It is conventional that such ceramic hybrid substrates are obtainable by laminating individual function layers that may have electrical connecting leads, integrated circuit constituents, micromechanical structures, etc. Such a sandwich arrangement that includes several function layers is subsequently sintered so that the finished ceramic hybrid substrate is formed. The finished ceramic hybrid substrate therefore has a surface structure that includes some ceramic surface areas and some metallic surface areas (conducting tracks, pads) embedded in them. By miniaturizing such ceramic hybrid substrates, the distance between adjacent metallic areas can be in the range of $< 100 \mu\text{m}$. In order to be able subsequently to contact such metallic surface areas integrated in the so-called fine line technology, for example, by bonding, the application of electrically conductive adhesives, etc., it is conventional that the metallic surface areas can be finished, for example, by applying a contact metal (silver, gold, or the like) to the metallic surface areas using a chemical deposition process. In this case, the ceramic hybrid

substrates are treated in chemical baths, some of which contain aggressive and etching substances that attack the surface of the ceramic surface areas. Moreover, it is disadvantageous that, during the deposition of the contact metal in chemical baths, deposits of metals can also occur on the ceramic surface areas which can - in particular in view of the small distances between the metallic surface areas - result in short circuits. Moreover, it is disadvantageous that during a subsequent contacting of the metallic surface areas, for example, by an electrically conductive adhesive, the adhesive tends to flow (bleed), so that short circuits can occur between adjacent metallic areas.

SUMMARY

In contrast, the method according to the present invention and the ceramic hybrid substrate according to the present invention provides the advantage that a subsequent machining of the metallic surface areas or a subsequent contacting of the metallic surface areas may occur, with a reduced tendency of short circuits between adjacent metallic surface areas. By esterifying the ceramic surface areas of the ceramic hybrid substrate, the ceramic surface areas may be protected selectively during the subsequent post-treatments in chemical baths. As a result of the esterification, a monomolecular surface layer is formed on the ceramic surface areas which is resistant to chemicals and heat, so that metal coatings chemically deposited in particular on the metallic surface areas are not able to deposit on the ceramic surface areas. Moreover, this selective esterifying of the ceramic surface areas causes a change in their surface tension, so that electrically conductive adhesives applied to the metallic surface areas do not tend to flow onto the ceramic surface areas.

The surface of the ceramic hybrid substrate may be treated with a solution including organic constituents tailored to the ceramic surface. This treatment may occur via a dipping bath,

flow wave soldering, spraying on, spreading on with a doctor,
etc. By wetting the surface with the solution including the
organic constituents, the solution is deposited in micropores
of the ceramic surface areas. Via a subsequent heat treatment,
crosslinking of the organic constituents of the solution with
lattice structures on the ceramic surface areas may occur.
This results in the formation of the chemically and thermally
stable (resistant) surface coating of the ceramic surface
areas. By a subsequent removal of non-crosslinked residues of
the solution including the organic constituents, the solution
may be removed from the metallic surface areas, where no
adhering effect (crosslinking) occurs. The metallic surface
areas in the processed form and with the original properties
are thus available for further processing.

An example method according to the present invention may be
used for ceramic hybrid substrates whose manufacture is
silicon-based, in which the ceramic surface areas are treated
with silicon as a solution containing an organic component
(siloxane). The concentrations of organic silicon compounds
may be between 0.1 and 1% of the solution - relative to the
total volume. Using such a treatment, a silicon oxide or
silicon dioxide surface layer that has good resistance to
chemical and thermal influences may be achieved after the
crosslinking of the solution with the ceramic surface areas.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 to 3 illustrate various phases of the treatment of
the ceramic surface areas.

Figures 4 and 5 schematically illustrate the esterification of
the ceramic surface areas.

DETAILED DESCRIPTION

In Figures 1 to 3, a ceramic hybrid substrate 10 (LTCC
microhybrid substrate) is illustrated schematically. Ceramic
hybrid substrate 10 includes ceramic surface areas 14 and

metallic surface areas 16 on its surface 12. Metallic surface areas 16 may, for example, be bonding pads, adhesive pads, etc. The processing of such ceramic hybrid substrates 10 is generally conventional, so that further details of this will not be further explained.

An example method according to the present invention for achieving a surface improvement of ceramic surface areas 14 is explained below.

First, as illustrated in Figure 1, surface 12 is acted upon by a solution 18 having organic components. Solution 18 may act, for example, via a dipping bath, spraying on, flow wave soldering, etc. This results in solution 18 being deposited on ceramic surface areas 14 and metallic surface areas 16. Excess quantities of solvent are removed mechanically, for example, by wiping off, blowing off, centrifuging, etc. This results in the formation of a thin layer of solution 18 on the entire surface 12, i.e., on ceramic surface areas 14 and metallic surface areas 16. Solution 18 adheres to surface 12 by surface tension and penetrates surface pores.

Solution 18 includes, for example, a 0.1% siloxane solution.

Figure 4 shows a ceramic surface area 14 of ceramic hybrid substrate 10 in section. Ceramic hybrid substrate 10 is made, for example, of a silicon glass ceramic. Such silicon glass ceramics have reactive groups (OH groups). Wetting with solution 18, which may contain silanes as organic components, is also illustrated in Figure 4.

Subsequently, a heat treatment of ceramic hybrid substrate 10 occurs, for example, at a temperature of about 100°C and for a period of about 30 minutes. This results in a silanization (etherification) of ceramic surface areas 14. The resulting crosslinking is illustrated in Figure 5. Silicon attaches itself to the reactive groups, forming an Si-O-Si structure.

Such silicon structures, as is conventional, excel by their chemically and thermally stable properties. Free hydroxyl groups (OH groups) as reactive groups react with the silicon-containing educt, resulting in the formation of the Si-O-Si bond (siloxanes).

Then, as illustrated in Figure 2, residual quantities 18" of solution 18 not crosslinked with ceramic surface areas 14 are removed.

This removal may be implemented by washing off with a solvent, for example, isopropanol. This results in the surface coating of ceramic surface areas 14 with silicon components 18', as illustrated in Figure 3. Metallic surface areas 16 do not react with the organic components, so that they are unchanged after residual quantities 18" have been detached chemically and mechanically.

Thermal decomposition of organic component R_3 may occur via a subsequent baking procedure, so that a silicon dioxide layer is formed in ceramic surface areas 14, as indicated in the lower structural representation in Figure 5.

As a result of the method according to the present invention, ceramic hybrid substrate 10 includes ceramic surface areas 14 that have a high chemical stability against etching attacks occurring in the subsequent manufacturing process. In particular, defective depositions on ceramic surface areas 14 situated between metallic surface areas 16 may be avoided with a subsequent deposition of metals, for example, silver, nickel, palladium, gold, etc., on metallic surface areas 16. Thus the danger of short circuits is reduced. Moreover, the surface tension of ceramic surface areas 14 is changed, such that electrically conductive adhesives applied to metallic surface areas 16 do not tend to flow, so that the formation of bridges, etc. between adjacent metallic surface areas 16 is likewise considerably reduced.

A modification of ceramic surface areas 14 provided according to the present invention may be integrated into the total manufacturing process of the circuit arrangement including ceramic hybrid substrates 10, to produce various process advances. According to a first example embodiment variant, silanization of ceramic surface areas 14 occurs after the manufacture of ceramic hybrid substrate 10, as illustrated in Figures 1 to 3, i.e., before subsequent thick-film processes, baking processes, plating processes, provision of substrate 10 with conductive adhesives, bonding, etc. In particular, a protective coating of ceramic surface areas 14 against chemical attacks in the chemical baths during plating (deposition of metals on metallic surface areas 16) is achieved.

According to another variant example embodiment according to the present invention, the silanization of ceramic surface areas 14 may occur after the thick-film processes and baking processes. Silanization may then occur before plating, conductive adhesive processes, or bonding. This results in the same advantages as in the first example embodiment variant.

Silanization of ceramic surface areas 14 may also occur after plating (metallization) of metallic surface areas 14. However, this does not provide a protective coating against the action of the chemical baths on ceramic surface areas 14. However, during a subsequent provision of substrates 10 with electrically conductive adhesives or bonding, for example, the flow of the adhesives is reduced by influencing the surface tension.

Depending on the desired processing, siloxanization of ceramic surface areas 14 may thus be incorporated at various points in time during processing.

Figure 1 consists of 12 histograms arranged in a single column. Each histogram represents the distribution of the number of non-zero elements in the vector x for a specific value of n . The x-axis for all histograms is labeled 'x' and ranges from 0 to 120. The y-axis is labeled 'count' and ranges from 0 to 100. The histograms are for $n = 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120$. As n increases, the distribution of x becomes more concentrated around zero, with the peak count increasing significantly.

5.

METHOD FOR THE SELECTIVE COATING OF CERAMIC SURFACE AREAS

FIELD OF THE INVENTION

The present invention relates to a method for treating the surface of a ceramic hybrid substrate [having] including ceramic surface areas and metallic surface areas.

[Background Information

] BACKGROUND INFORMATION

The use of ceramic (glass ceramic) hybrid substrates is [known] conventional, for example [for], in the construction of electrical circuit arrangements. Such electrical circuit arrangements are used in various industrial areas, for example, in the area of motor vehicle electronics for engine control, anti-lock braking control, [or the like] etc. The ceramic hybrid substrates contain processed electronic components and metallic conducting tracks, via which contacting of the hybrid substrates can occur. It is [known] conventional that such ceramic hybrid substrates are obtainable by laminating individual function layers [which] that may have electrical connecting leads, integrated circuit constituents, micromechanical structures [or the like], etc. Such a sandwich arrangement that includes several function layers is subsequently sintered so that the finished ceramic hybrid substrate is formed. The finished ceramic hybrid substrate therefore has a surface structure that includes some ceramic surface areas and some metallic surface areas (conducting tracks, pads) embedded in them. By miniaturizing such ceramic hybrid substrates, the distance between adjacent metallic areas can be in the range of $< 100 \mu\text{m}$. In order to be able subsequently to contact such metallic surface areas integrated in the so-called fine line technology, for example, by bonding, the application of electrically conductive

adhesives, [or the like] etc., it is [known] conventional that the metallic surface areas can be finished, for example, by applying a contact metal (silver, gold, or the like) to the metallic surface areas using a chemical deposition process. In this case, the ceramic hybrid substrates are treated in chemical baths, some of which contain aggressive and etching substances [which] that attack the surface of the ceramic surface areas. Moreover, it is disadvantageous that, during the deposition of the contact metal in chemical baths, deposits of metals can also occur on the ceramic surface areas which can - in particular in view of the small distances between the metallic surface areas - result in short circuits. Moreover, it is disadvantageous that during a subsequent contacting of the metallic surface areas, for example, by an electrically conductive adhesive, the adhesive tends to flow (bleed), so that short circuits can [likewise] occur between adjacent metallic areas.

[Summary of the Invention

] SUMMARY

In contrast, the method according to the present invention [having the features as recited in the preamble of Claim 1] and the ceramic hybrid substrate according to the present invention [having the features as recited in the preamble of Claim 16 offer] provides the advantage that a subsequent machining of the metallic surface areas or a subsequent contacting of the metallic surface areas may [take place] occur, with a reduced tendency [to] of short circuits between adjacent metallic surface areas. By esterifying the ceramic surface areas of the ceramic hybrid substrate, [it is advantageously achieved that] the ceramic surface areas [are] may be protected selectively during the subsequent post-treatments in chemical baths. As a result of the esterification, a monomolecular surface layer is formed on the ceramic surface areas which is resistant to chemicals and

heat, so that metal coatings chemically deposited in particular on the metallic surface areas are not able to deposit on the ceramic surface areas. Moreover, this selective esterifying of the ceramic surface areas causes a change in their surface tension, so that electrically conductive adhesives applied to the metallic surface areas do not tend to flow onto the ceramic surface areas.

The surface of the ceramic hybrid substrate [is preferably] may be treated with a solution [having] including organic constituents tailored to the ceramic surface. This treatment [preferably takes place] may occur via a dipping bath, flow wave soldering, spraying on, spreading on with a doctor, [or the like] etc. By wetting the surface with the solution [having] including the organic constituents, the solution is deposited in micropores of the ceramic surface areas. Via a [preferably provided] subsequent heat treatment, crosslinking of the organic constituents of the solution with lattice structures on the ceramic surface areas [takes place] may occur. This results in the formation of the chemically and thermally stable (resistant) surface coating of the ceramic surface areas. By a subsequent removal of non-crosslinked residues of the solution [having] including the organic constituents [preferably provided], the solution [is] may be removed from the metallic surface areas, where no adhering effect (crosslinking) [takes place] occurs. The metallic surface areas in the processed form and with the original properties are thus available for further processing.

[A preferred use of the] An example method according to the present invention [is] may be used for ceramic hybrid substrates whose manufacture is silicon-based, in which the ceramic surface areas [is] are treated with silicon as a solution containing an organic component (siloxane). The concentrations of organic silicon compounds [are preferably]

may be between 0.1 and 1% of the solution - relative to the total volume. Using such a treatment, a silicon oxide or silicon dioxide surface layer that has good resistance to chemical and thermal influences may be achieved after the crosslinking of the solution with the ceramic surface areas.

[Further preferred developments of the present invention appear from the other features recited in the subclaims.

Brief Description of the Drawing

The present invention is explained in more detail below with reference to exemplary embodiments illustrated in the related drawing.]

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 [through] to 3 [show] illustrate various phases of the treatment of the ceramic surface areas[and].

Figures 4 and 5 schematically [show] illustrate the esterification of the ceramic surface areas.

[Detailed Description of the Exemplary Embodiments

] DETAILED DESCRIPTION

In Figures 1 [through] to 3, a ceramic hybrid substrate 10 (LTCC microhybrid substrate) is [shown] illustrated schematically. Ceramic hybrid substrate 10 [has] includes ceramic surface areas 14 and metallic surface areas 16 on its surface 12. Metallic surface areas 16 may, for example, be bonding pads, adhesive pads, [or the like] etc. The processing of such ceramic hybrid substrates 10 is generally [known] conventional, so that further details of this will not be further explained [within the bounds of the present description].

[The] An example method according to the present invention for achieving a surface improvement of ceramic surface areas 14 is explained below.

5 First, as [indicated] illustrated in Figure 1, surface 12 is acted upon by a solution 18 having organic components. Solution 18 may act, for example, via a dipping bath, spraying on, flow wave soldering, [or the like] etc. This results in solution 18 being deposited on ceramic surface areas 14 and
10 metallic surface areas 16. Excess quantities of solvent are removed mechanically, for example, by wiping off, blowing off, centrifuging, [or the like] etc. This results in the formation of a thin layer of solution 18 on the entire surface 12, i.e., on ceramic surface areas 14 and metallic surface areas 16.
15 Solution 18 adheres to surface 12 by surface [tensions] tension and penetrates surface pores.

Solution 18 includes, for example, a 0.1% siloxane solution.

20 Figure 4 shows a ceramic surface area 14 of ceramic hybrid substrate 10 in section. Ceramic hybrid substrate 10 is made, for example, of a silicon glass ceramic. Such silicon glass ceramics have reactive groups (OH groups). Wetting with solution 18, which [in the specific exemplary embodiments
25 contains] may contain silanes as organic components, is also [shown] illustrated in Figure 4.

Subsequently, a heat treatment of ceramic hybrid substrate 10 [takes place] occurs, for example, at a temperature of about
30 100°C and for a period of about 30 minutes. This results in a silanization (etherification) of ceramic surface areas 14. The resulting crosslinking is [shown] illustrated in Figure 5. Silicon attaches itself to the reactive groups, forming an Si-O-Si structure. Such silicon structures, as is [known]
35 conventional, excel by their chemically and thermally stable

properties. Free hydroxyl groups (OH groups) as reactive groups react with the silicon-containing educt, resulting in the formation of the Si-O-Si bond (siloxanes).

5 Then, as [shown] illustrated in Figure 2, residual quantities 18" of solution 18 not crosslinked with ceramic surface areas 14 are removed.

10 This removal [is preferably] may be implemented by washing off with a solvent, for example, isopropanol. This results in the surface coating of ceramic surface areas 14 with silicon components 18' [shown], as illustrated in Figure 3. Metallic surface areas 16 do not react with the organic components, so that []they[] are unchanged after residual quantities 18" have been detached chemically and mechanically.

15 Thermal decomposition of organic component R₃ may [take place] occur via a subsequent baking procedure, so that a silicon dioxide layer is formed in ceramic surface areas 14, as indicated in the lower structural representation in Figure 5.

20 As a result of the method according to the present invention, ceramic hybrid substrate 10 [has] includes ceramic surface areas 14 that have a high chemical stability against etching attacks occurring in the subsequent manufacturing process. In particular, defective depositions on ceramic surface areas 14 situated between metallic surface areas 16 may be avoided with a subsequent deposition of metals, for example [of], silver, nickel, palladium, gold, [or the like] etc., on metallic surface areas 16. Thus the danger of short circuits is reduced. Moreover, the surface tension of ceramic surface areas 14 is changed, such that electrically conductive adhesives applied to metallic surface areas 16 do not tend to flow, so that the formation of bridges [or the like], etc.

between adjacent metallic surface areas 16 is likewise considerably reduced.

[The] A modification of ceramic surface areas 14 provided according to the present invention may be integrated into the total manufacturing process of the circuit arrangement [having] including ceramic hybrid substrates 10, to produce various process advances. According to a first example embodiment variant, silanization of ceramic surface areas 14 [takes place] occurs after the manufacture of ceramic hybrid substrate 10 [shown], as illustrated in Figures 1 to 3, i.e., before subsequent thick-film processes, baking processes, plating processes, provision of substrate 10 with conductive adhesives, bonding, [or the like] etc. In particular, a protective coating of ceramic surface areas 14 against chemical attacks in the chemical baths during plating (deposition of metals on metallic surface areas 16) is achieved [here].

According to [a further] another variant example embodiment according to the present invention, the silanization of ceramic surface areas 14 may [take place] occur after the thick-film processes and baking processes. Silanization may then [takes place] occur before plating, conductive adhesive processes, or bonding. This results in the same advantages as in the first example embodiment variant.

[Finally, silanization] Silanization of ceramic surface areas 14 may also [take place] occur after plating (metallization) of metallic surface areas 14. However, this does not provide a protective coating against the action of the chemical baths on ceramic surface areas 14. However, during a subsequent provision of substrates 10 with electrically conductive adhesives or bonding, for example, the flow of the adhesives is reduced by influencing the surface tension.

Depending on the desired processing, siloxanization of ceramic surface areas 14 may thus be incorporated at various points in time during processing.

20430-620001

[Abstract

] **ABSTRACT**

[A] In a ceramic hybrid substrate and a method for treating
the surface of a ceramic hybrid substrate having ceramic
5 surface areas and metallic surface areas [is described.

The], the ceramic surface areas [(14)] are esterified. [

10 (Figure 4)]

20450-6XCE001

1/PRTS

[10191/2180]

METHOD FOR THE SELECTIVE COATING OF CERAMIC SURFACE AREAS

The present invention relates to a method for treating the surface of a ceramic hybrid substrate having ceramic surface areas and metallic surface areas.

5 Background Information

10 The use of ceramic (glass ceramic) hybrid substrates is known for example for the construction of electrical circuit arrangements. Such electrical circuit arrangements are used in various industrial areas, for example in the area of motor vehicle electronics for engine control, anti-lock braking control, or the like. The ceramic hybrid substrates contain processed electronic components and metallic conducting tracks, via which contacting of the hybrid substrates can occur. It is known that such ceramic hybrid substrates are obtainable by laminating individual function layers which may have electrical connecting leads, integrated circuit constituents, micromechanical structures or the like. Such a sandwich arrangement that includes several function layers is subsequently sintered so that the finished ceramic hybrid substrate is formed. The finished ceramic hybrid substrate therefore has a surface structure that includes some ceramic surface areas and some metallic surface areas (conducting tracks, pads) embedded in them. By miniaturizing such ceramic hybrid substrates, the distance between adjacent metallic areas can be in the range of $< 100 \mu\text{m}$. In order to be able subsequently to contact such metallic surface areas integrated in the so-called fine line technology, for example by bonding, the application of electrically conductive adhesives, or the like, it is known that the metallic surface areas can be finished, for example by applying a contact metal (silver, gold, or the like) to the metallic surface areas using a chemical deposition process. In this case, the ceramic hybrid

substrates are treated in chemical baths, some of which contain aggressive and etching substances which attack the surface of the ceramic surface areas. Moreover, it is disadvantageous that during the deposition of the contact metal in chemical baths, deposits of metals can also occur on the ceramic surface areas which can - in particular in view of the small distances between the metallic surface areas - result in short circuits. Moreover it is disadvantageous that during a subsequent contacting of the metallic surface areas, for example by an electrically conductive adhesive, the adhesive tends to flow (bleed), so that short circuits can likewise occur between adjacent metallic areas.

Summary of the Invention

In contrast, the method according to the present invention having the features as recited in the preamble of Claim 1 and the ceramic hybrid substrate according to the present invention having the features as recited in the preamble of Claim 16 offer the advantage that a subsequent machining of the metallic surface areas or a subsequent contacting of the metallic surface areas may take place, with a reduced tendency to short circuits between adjacent metallic surface areas. By esterifying the ceramic surface areas of the ceramic hybrid substrate, it is advantageously achieved that the ceramic surface areas are protected selectively during the subsequent post-treatments in chemical baths. As a result of the esterification, a monomolecular surface layer is formed on the ceramic surface areas which is resistant to chemicals and heat, so that metal coatings chemically deposited in particular on the metallic surface areas are not able to deposit on the ceramic surface areas. Moreover, this selective esterifying of the ceramic surface areas causes a change in their surface tension, so that electrically conductive adhesives applied to the metallic surface areas do not tend to flow onto the ceramic surface areas.

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The surface of the ceramic hybrid substrate is preferably treated with a solution having organic constituents tailored to the ceramic surface. This treatment preferably takes place via a dipping bath, flow wave soldering, spraying on, spreading on with a doctor, or the like. By wetting the surface with the solution having the organic constituents, the solution is deposited in micropores of the ceramic surface areas. Via a preferably provided subsequent heat treatment, crosslinking of the organic constituents of the solution with lattice structures on the ceramic surface areas takes place. This results in the formation of the chemically and thermally stable (resistant) surface coating of the ceramic surface areas. By a subsequent removal of non-crosslinked residues of the solution having the organic constituents preferably provided the solution is removed from the metallic surface areas, where no adhering effect (crosslinking) takes place. The metallic surface areas in the processed form and with the original properties are thus available for further processing.

A preferred use of the method according to the present invention is for ceramic hybrid substrates whose manufacture is silicon-based, in which the ceramic surface areas is treated with silicon as a solution containing an organic component (siloxane). The concentrations of organic silicon compounds are preferably between 0.1 and 1% of the solution - relative to the total volume. Using such a treatment, a silicon oxide or silicon dioxide surface layer that has good resistance to chemical and thermal influences may be achieved after the crosslinking of the solution with the ceramic surface areas.

Further preferred developments of the present invention appear from the other features recited in the subclaims.

Brief Description of the Drawing

The present invention is explained in more detail below with reference to exemplary embodiments illustrated in the related drawing.

Figures 1 through 3 show various phases of the treatment of the ceramic surface areas and

Figures 4 and 5 schematically show the esterification of the ceramic surface areas.

Detailed Description of the Exemplary Embodiments

In Figures 1 through 3, a ceramic hybrid substrate 10 (LTCC microhybrid substrate) is shown schematically. Ceramic hybrid substrate 10 has ceramic surface areas 14 and metallic surface areas 16 on its surface 12. Metallic surface areas 16 may, for example, be bonding pads, adhesive pads, or the like. The processing of such ceramic hybrid substrates 10 is generally known, so that further details of this will not be explained within the bounds of the present description.

The method according to the present invention for achieving a surface improvement of ceramic surface areas 14 is explained below.

First, as indicated in Figure 1, surface 12 is acted upon by a solution 18 having organic components. Solution 18 may act for example via a dipping bath, spraying on, flow wave soldering, or the like. This results in solution 18 being deposited on ceramic surface areas 14 and metallic surface areas 16. Excess quantities of solvent are removed mechanically, for example by wiping off, blowing off, centrifuging, or the like. This results in the formation of a thin layer of solution 18 on the entire surface 12, i.e., on ceramic surface areas 14 and metallic surface areas 16. Solution 18 adheres to surface 12 by surface tensions and penetrates surface pores.

Solution 18 includes for example a 0.1% siloxane solution.

Figure 4 shows a ceramic surface area 14 of ceramic hybrid substrate 10 in section. Ceramic hybrid substrate 10 is made for example of a silicon glass ceramic. Such silicon glass ceramics have reactive groups (OH groups). Wetting with solution 18, which in the specific exemplary embodiments contains silanes as organic components, is also shown in Figure 4.

Subsequently a heat treatment of ceramic hybrid substrate 10 takes place, for example at a temperature of about 100°C and for a period of about 30 minutes. This results in a silanization (etherification) of ceramic surface areas 14. The resulting crosslinking is shown in Figure 5. Silicon attaches itself to the reactive groups, forming an Si-O-Si structure. Such silicon structures, as is known, excel by their chemically and thermally stable properties. Free hydroxyl groups (OH groups) as reactive groups react with the silicon-containing educt, resulting in the formation of the Si-O-Si bond (siloxanes).

Then, as shown in Figure 2, residual quantities 18" of solution 18 not crosslinked with ceramic surface areas 14 are removed.

This removal is preferably implemented by washing off with a solvent, for example isopropanol. This results in the surface coating of ceramic surface areas 14 with silicon components 18' shown in Figure 3. Metallic surface areas 16 do not react with the organic components, so that they are unchanged after residual quantities 18" have been detached chemically and mechanically.

Thermal decomposition of organic component R₃ may take place via a subsequent baking procedure, so that a silicon dioxide

layer is formed in ceramic surface areas 14, as indicated in the lower structural representation in Figure 5.

As a result of the method according to the present invention, ceramic hybrid substrate 10 has ceramic surface areas 14 that have a high chemical stability against etching attacks occurring in the subsequent manufacturing process. In particular, defective depositions on ceramic surface areas 14 situated between metallic surface areas 16 may be avoided with a subsequent deposition of metals, for example of silver, nickel, palladium, gold, or the like, on metallic surface areas 16. Thus the danger of short circuits is reduced. Moreover, the surface tension of ceramic surface areas 14 is changed such that electrically conductive adhesives applied to metallic surface areas 16 do not tend to flow, so that the formation of bridges or the like between adjacent metallic surface areas 16 is likewise considerably reduced.

The modification of ceramic surface areas 14 provided according to the present invention may be integrated into the total manufacturing process of the circuit arrangement having ceramic hybrid substrates 10, to produce various process advances. According to a first embodiment variant, silanization of ceramic surface areas 14 takes place after the manufacture of ceramic hybrid substrate 10 shown in Figures 1 to 3, i.e., before subsequent thick-film processes, baking processes, plating processes, provision of substrate 10 with conductive adhesives, bonding, or the like. In particular, a protective coating of ceramic surface areas 14 against chemical attacks in the chemical baths during plating (deposition of metals on metallic surface areas 16) is achieved here.

According to a further variant, the silanization of ceramic surface areas 14 may take place after the thick-film processes and baking processes. Silanization then takes place before

plating, conductive adhesive processes, or bonding. This results in the same advantages as in the first variant.

5 Finally, silanization of ceramic surface areas 14 may also
take place after plating (metallization) of metallic surface
areas 14. However, this does not provide a protective coating
against the action of the chemical baths on ceramic surface
areas 14. However, during a subsequent provision of substrates
10 with electrically conductive adhesives or bonding, for
example, the flow of the adhesives is reduced by influencing
the surface tension.

15 Depending on the desired processing, siloxanization of ceramic
surface areas 14 may thus be incorporated at various points in
time during processing.

What is claimed is:

1. A method for treating the surface of a ceramic hybrid substrate having ceramic surface areas and metallic surface areas,
wherein the ceramic surface areas (14) are esterified.
2. The method according to Claim 1,
wherein the ceramic surface areas (14) are treated with a solution (18) having organic constituents tailored to the ceramic structure.
3. The method according to one of the preceding claims,
wherein the ceramic structure is manufactured on the basis of silicon and the solution contains silicon.
4. The method according to one of the preceding claims,
wherein a siloxane solution is used as solution (18).
5. The method according to Claim 4,
wherein the solution contains between 0.1 and 1% of siloxane and 99.9 to 99% of isopropanol - relative to 100% total volume.
6. The method according to one of the preceding claims,
wherein the solution (18) is applied by dip coating.
7. The method according to one of Claims 1 through 5,
wherein the solution (18) is applied by spraying on.
8. The method according to one of the preceding claims,
wherein the excess solution (18) is removed mechanically.
9. The method according to Claim 8,
wherein the excess solution (18) is wiped off.
10. The method according to Claim 8,

wherein the excess solution (18) is blown off.

11. The method according to one of the preceding claims, wherein the surface contacted by the solution is heat-treated.

12. The method according to Claim 11, wherein the heat treatment takes place at a temperature of about 100°C.

13. The method according to one of the preceding claims, wherein the heat treatment takes place for a period of between 0.4 and 0.6 hours.

14. The method according to one of the preceding claims, wherein solution constituents (18") not crosslinked after the heat treatment are removed.

15. The method according to Claim 14, wherein solution constituents (18") not crosslinked are washed off.

16. A ceramic hybrid substrate with a surface having ceramic surface areas and metallic surface areas, wherein the ceramic surface areas (14) are esterified.

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(Figure 4)

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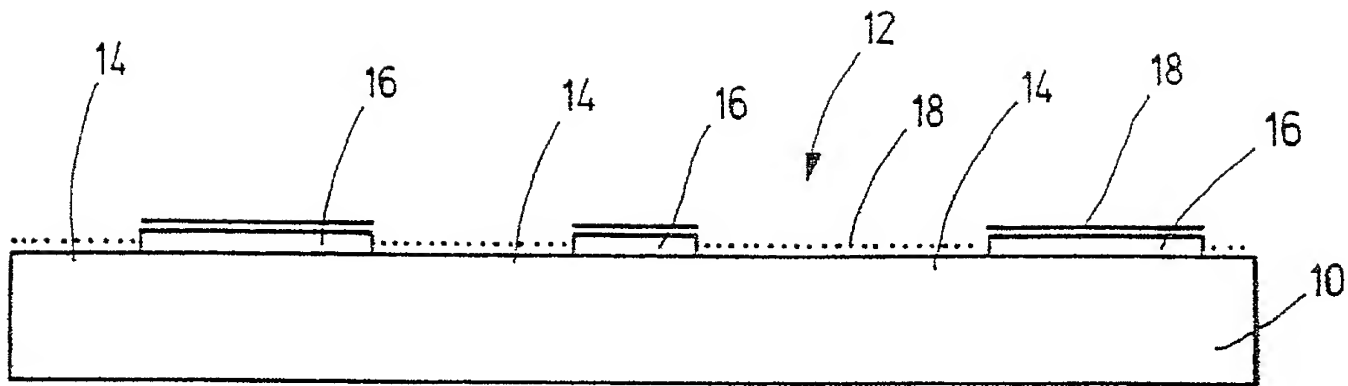


Fig. 1

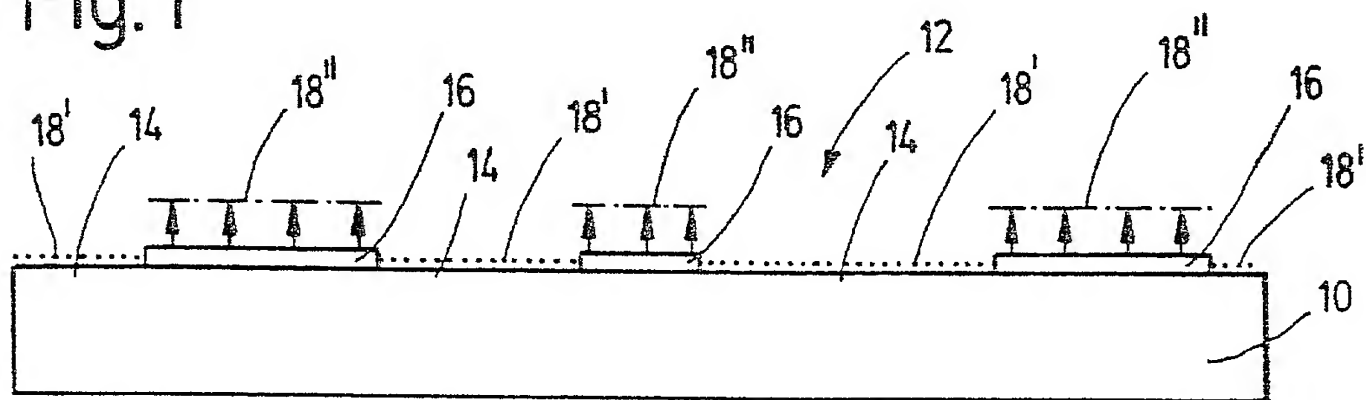


Fig. 2

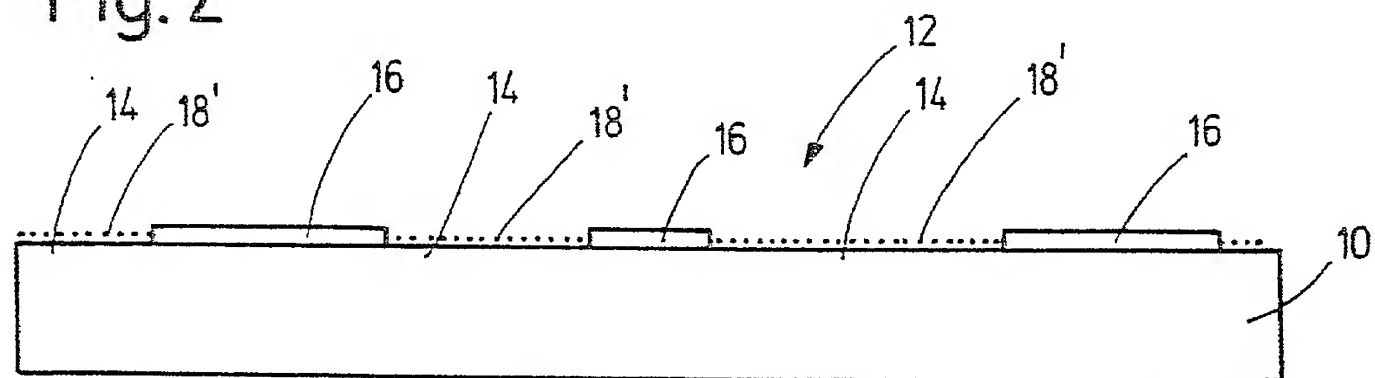
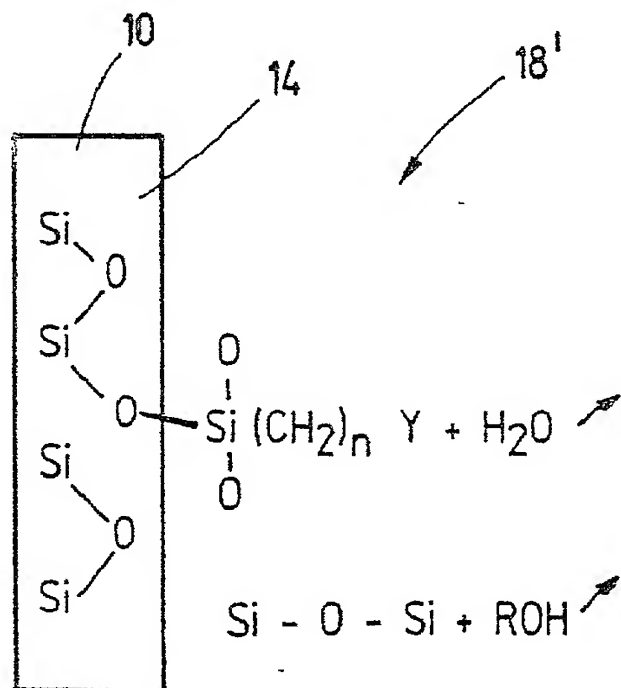
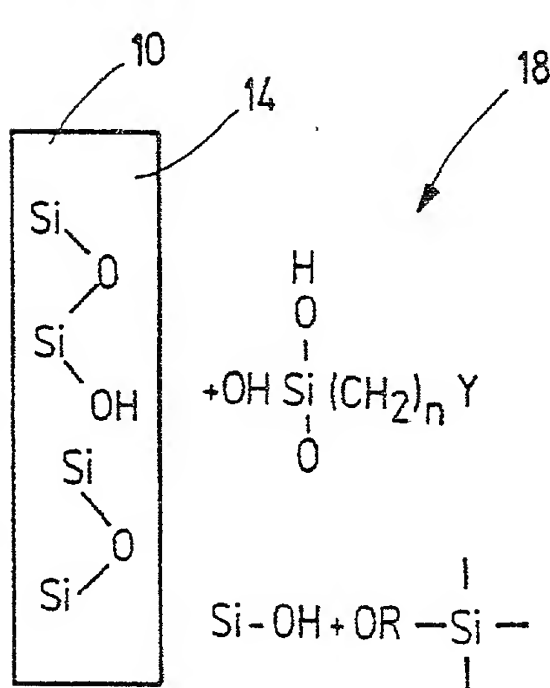


Fig. 3



DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **METHOD FOR THE SELECTIVE COATING OF CERAMIC SURFACE AREAS**, the specification of which was filed as International Application **PCT/DE00/02023** on June 21, 2000;

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application(s) for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

EL244510277

PRIOR FOREIGN APPLICATION(S)

Number	Country filed	Day/month/year	Priority Claimed Under 35 USC 119
199 30 782.2	Fed. Rep. of Germany	03 July 1999	Yes

And I hereby appoint Richard L. Mayer (Reg. No. 22,490) and Gerard A. Messina (Reg. No. 35,952) my attorneys with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

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Please direct all telephone calls to Richard L. Mayer at (212) 425-7200.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful and false statements may jeopardize the validity of the application or any patent issued thereon.

Inventor: Walter ROETHLINGSHOEFER

1-00
Inventor's Signature: *Walter Roethlingshoefer*

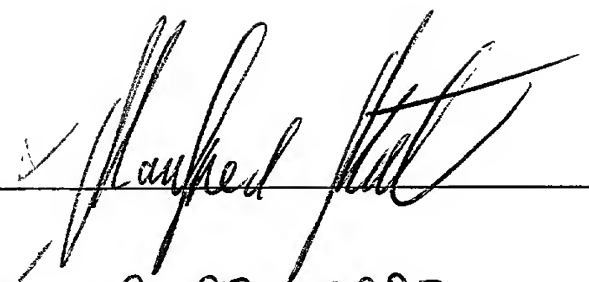
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